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RADIOLYTIC HYDROLYSIS OF CELLULOSE

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RADIOLYTIC HYDROLYSIS OF CELLULOSE

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

In an attempt to solve the problem of solid waste disposal, this study examines the conversion of cellulosic wastes to protein. This report published by the National Environmental Research Center - Cincinnati evaluated methods of acid hydrolysis and intense irradiation that effect the conversion of cellulose to protein.

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Research Center - Cincinnati

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16. Abstracts Methods of drastic acid hydrolysis or of intense irradiation can effect the conversion of cellulose to glucose; however, either of these two processes is not practical for a large-scale commercial operation. An investigation was made using a combination of the two above mentioned methods. Cellulose (filter paper) was irradiated with gamma rays and subsequently hydrolyzed in solutions of hydrochloric acid. The combination of possible industrial conditions, i.e., dilute acid hydrolysis, moderate radiation doses, short hydrolysis times, and relatively low temperatures, produced cellulose-to-glucose yields of up to 25%. Although the yields obtained were too low to be industrially attractive, this study indicated promising trends toward cellulose conversion under radiation and hydrolysis conditions that might well lie within the range of economic feasibility.

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SUMMARY STATEMENT

Cellulose is a polysaccharide and as such is a source of glucose. However, even though cellulose is the most abundant of all naturally occurring organic compounds, it remains essentially nonnutritional. Methods of drastic acid hydrolysis or intense irradiation can effect the conversion of cellulose to gluclose; however, either of these two processes is not practical for a large-scale commercial operation.

An investigation was made using a combination of the two above mentioned methods. Cellulose (filter paper) was irradiated with gamma rays and subsequently hydrolyzed in solutions of hydrochloric acid. The combination of possible industrial conditions, i.e., dilute acid (< 10% HCl) hydrolysis, moderate radiation doses (5×10^6 rads), short hydrolysis times (< 20 hours), and relatively low temperatures (25 to 90°C), produced cellulose-to-glucose yields of up to 25%. Although the yields obtained were too low to be industrially attractive, this study indicated promising trends toward cellulose conversion under radiation and hydrolysis conditions that might well lie within the range of economic feasibility.

I. INTRODUCTION

Municipal and industrial cellulose wastes, along with agricultural wastes, serve as potential resources for millions of tons of protein a year. (Cellulose is a source of glucose, which, in turn, can be converted to protein.) Presently these wastes are eliminated by burning and lagooning. The first method of disposal causes air pollution problems and the second leads to odor and insect problems plus the ever increasing unavailability of free space for the ponds.

It is possible to convert cellulose to glucose by a hydrolysis process. However, unusually long hydrolysis runs are necessary to assure significant conversion of cellulose to glucose, due to the high percentage of crystalline (acid stable) as opposed to amorphous (acid labile) regions in the cellulose structure (4). This represents the transition of the cellulose chain from an orderly arrangement in the direction of the microfibrils in the crystalline region to the less orderly orientation of the molecular chain in the amorphous region. The high degree of crystallinity is believed to be associated with hydrogen bond formation between hydroxyl groups of adjacent molecules. These strong intermolecular forces are sufficient to permit considerable expansion of the unit cell without disruption during swelling (solution of the solvent in the polymer phase) by strong acids and alkalis. Thus the crystalline areas of cellulose are almost unreactive toward <u>most</u> liquid systems. Cellulose is dissolved by cuprammonium hydroxide, cupriethylene-diamine, quaternary ammonium hydroxides, concentrated aqueous zinc chloride, 70% sulfuric acid, 40% hydrochloric acid and syrupy phosphoric acid (26). Viscosity studies employ the first two mentioned solvents and the remaining solvents in the specified concentrations, if any, have been previously studied. While these laboratory findings are intriguing, none of them has, up to now, attained a level of commercial feasibility. Costs associated with the required physical or chemical processing have been too high relative to the value of the products derived.

For example, as early as the nineteenth century Braconnot (5) postulated that the complete hydrolysis by acid of cellulose gave rise to

glucose. In the first part of this century, Monier-Williams (15) treated cotton cellulose at room temperature for one week with 72% sulfuric acid. He then diluted the mixture to an acidity of less than 1% and, boiled the solution for fifteen hours and from the hydrolyzate of his experiments he isolated over 90% of the theoretical amount of pure glucose. His analytical data, based on optical rotation and on copper reduction, showed the presence of about 94.5% of glucose in the solutions.

Between Braconnot's investigation in 1819 and those of Monier-Williams a number of other researchers studied the hydrolysis reaction (10, 16, 17, 28, 29). All obtained 60% to 97% glucose yield and all used processes of laboratory interest only.

Cellulose is a polysaccharide consisting of glucose anhydride units linked together through the 1 and 4 carbon atoms with a β-glucoside linkage. This β-glucoside link is labile towards the hydrolytic agents mentioned earlier and continued exposure to such reagents leads to progressive reduction in the molecular weight leading ultimately to the disaccharide, cellobiose (which is composed of two glucose units) and to glucose itself.

Gamma radiation also has a degrading effect on the cellulose chain. However, gamma radiation cannot distinguish between the crystalline and amorphous regions of the cellulose structure and degrades both equally as well, producing glucose along with new amorphous regions.

From the extensive studies already made it seems that neither hydrolysis nor radiation alone can attain conversion levels that would make the process industrially feasible for glucose production. However, by using radiation to disrupt the crystalline regions of the cellulose structure so that they "appear" amorphous to the acid in hydrolysis, a combination of the two procedures, under the proper conditions of dose, temperature, acid strength and duration of hydrolysis causes a significant increase in sugar yield. For this reason an optimum combination of the two procedures was sought, one that could utilize water radiation sources and make cellulose an actual rather than a potential source of glucose.

II. CHEMICAL CONSIDERATIONS

Hydrolytic degradation of the cellulose chains results when cellulose is placed in acid. In this reaction the acid serves as a catalyst which promotes the breaking of the β-glucoside bonds by the addition of a water molecule to the cellulose chain (6).

When very dilute acid (< 1%) is used for the hydrolysis of cellulose, there is no evidence of humus production from unhydrolyzed cellulose as is common when concentrated (> 50%) acids are employed, but the products of hydrolysis may decompose at almost the same rate that cellulose is hydrolyzed. In the work by Kressman (11) this decomposition was studied and its control permitted the increase of fermentable sugar. The maximum yield of sugar in one treatment resulted after a short hydrolysis (< 4 hours), further heating resulting in decomposition of the sugar as fast as it was formed. If the reaction were continued long enough, Kressman found that the cellulose would be hydrolyzed completely and all the resulting sugar decomposed.

These studies were conducted at high temperatures, greater than the boiling point of the acid solution used. In the presence of dilute acids the reaction itself is much more complex than those in the presence of acids that dissolve cellulose. The reaction has been found to be heterogeneous and depends on contact and the ability of the liquid to enter the crystalline structure (27).

Aside from the consequent formation of humic substances, hydrolysis of cellulose with concentrated acids is also complicated by the formation of condensation or reversion products to low polymers (27). If glucose were formed, it would be converted into polymers that are believed to have linkages differeing from the original 1, 4 linkages. These polymers are water-soluble and behave as the oligosaccharides or intermediate products from cellulose. By heating glucose polymers or the oligosaccharides with dilute acid, simple sugars are produced. If allowed to stand in strong acid, or if heated, both the oligosaccharides and glucose polymers form humic acid type products.

Thus, it can generally be said tha concentrated acids at low (25°C) temperatures favor higher conversion of cellulose with less decomposition of the resulting sugar than very dilute acids at high temperatures. Much of the randomly oriented, more open network of molecular segments in the amorphous portion will be more accessible to acids and oxidants than the interior of the systematically arranged denser crystallites, and in consequence, the course of the degradation may depend to a marked extent upon the physical characteristics of the sample, as well as upon the chemical nature of the reagent (26).

In considering the effects of radiation on the hydrolysis reaction, gamma radiation is most commonly used because of its high penetrating capacity, the possibility of obtaining relatively nigh radiation dose rates, and the fact that it does not result in induced radioactivity. In this consideration, the absorbed energy of the radiation results in ionization and excitation of the molecules present in the system (25). From a chemical point of view, this can eventually lead to processes which correspond to dissociation of the corresponding bond, thus resulting in degradation and depolymerization.

Recent studies (2, 3, 12, 18, 22) on the high-energy irradiation of cellulose have indicated that oxidative reactions occur. The cellulose molecules were altered by chain cleavage and the formation of reducing and acid groups. It should be emphasized before proceeding further that these reported observations were obtained using pure cotton or wood pulp, and no samples were used that had lignin present. The lignin component of wood was observed to be comparatively unaffected after 3×10^8 rads in experiments performed by Lawton, et al. (13). The data suggest that the lignin protects wood and prevents hydrolysis or digestion in the presence of radiation.

The fact that the products of radiolysis tend to be far more specific than would be expected from a random distribution of ionizations or excitations in the irradiated molecule suggests that the site at which a chemical bond is broken is not necessarily the site at which the energy absorption occurred initially. That is, it seems likely that the energy absorbed

in a given portion of a molecule can migrate within that molecule. It was found that such transport of energy can be effective over large distances (1).

Cotton cellulose is made up of repeating anhydroglucose units, which contain carbon, oxygen and hydrogen atoms. Based on the above mentioned specificity, each anhydroglucose monomer unit has an equal probability of being affected by the radiation, and each carbon and oxygen atom of this unit has at least a similar probability of being ionized.

Saeman, et al. (18) found that irradiation caused a steady decrease in the molecular weight (as evidenced by a decrease in viscosity) and, after doses of ca. 5×10^8 rads, the cellulose was converted into a water-soluble material. The rate of main-chain degradation was approximately the same for cotton linters and for wood pulp. Such a behavior contrasts with the resistance of these two species of cellulose to heterogeneous hydrolyses, cotton linters being much more stable than wood pulp, and where the resistant portion of unirradiated wood pulp hydrolyzes at approximately twice the rate shown by the resistant portion of unirradiated cotton linters. This behavior suggests that depolymerization is not affected by crystalline organization.

Generally, the various types of high-energy radiation seemed to produce the same over-all effects on cellulose. The total dosage, and not the dose rate, seemed to be the most important factor. The absence or presence of moisture in the cellulose irradiated did, under certain conditions, alter the effect. The influence of water on the radiation stability of cellulose was investigated by Glegg and Kertesz (8). These authors found that the rate of degradation of cotton and wood pulp was the same for water content in the range of 3.3 to 5.6%. At lower moisture levels (e.g., at 0.26%) an important after-effect was observed, characterized by a steady decrease of the intrinsic viscosity after irradiation. The gaseous atmosphere under which the irradiation was carried out seemed to produce only small differences in the various properties studied. Blouin and Arthur (2) found the same type of degradation in a nitrogen atmosphere as in an oxygen atmosphere with oxygen producing only slight enhancement of the reaction. Recall

also that no difference arises in the rate of fracture as between crystalline and amorphous regions. There is no tendency for the cellulose chain to be first broken in the amorphous regions and only subsequently in the crystalline ones as in the case when depolymerization or degradation is induced by chemical means.

As was mentioned previously, very little work has been done on the combined effects of radiation and hydrolysis. In one of the few recent studies, Saeman et al. (18) found that the rate of hydrolysis of irradiated cellulose by dilute acid solutions at very high temperatures ($\sim$ 175°C) steadily increased with dose. The authors further concluded from the kinetics of this hydrolysis that irradiation partly destroyed the crystalline regions in the polymer, thus favoring the penetration of the reagents in the bulk of the material.

III. EXPERIMENTAL PROCEDURE

For the purposes of this study, the cellulose chosen for all irradiations and hydrolysis experimentation was an ashless grade of filter paper--a form of cotton cellulose. In its manufacturing preparation this filter paper was double washed with hydrochloric and hydrofluoric acid and therefore no further purification procedures were executed. The acid chosen for the hydrolysis procedure was hydrochloric, reagent grade. The other commonly known acids were eliminated because of their distinct disadvantages. Sulfuric acid was discounted for four reasons: its use may introduce sulfate groups which could enable the residual cellulose to be peptized and hence partly dissolved during washing (14); any industrial process using sulfuric acid involves problems in recovery; the amount of acid required is large, and (lastly) sulfuric acid, more than any other, has been studied to no apparent success. Because of their corrosive ability, derivative formation and recovery problems, hydrofluoric, formic and phosphoric acids were not considered. Alkalies were disregarded because of the degradation effects on cellulose with little or no consequent sugar production.

The acid strengths initially studied were 0.4%, 1.6%, 3.75% and 7.5%. Moderately dilute acids were chosen over concentrated solutions because they do not form humic compounds and do not afford the glucose products the proper medium for recombining into polymers having linkages differing from the original 1.4 linkages, as do concentrated acids.

The University of Virginia Reactor (swimming-pool type) was used at its rated capacity (1 mw) to perform the irradiations. Although the core is a source of fast and thermal neutrons and gamma rays, the hydrogen in the water and a cadmium foil served to shield the cellulose samples from the neutrons. Thus for practical purposes the samples were effectively irradiated by gamma radiation. A rate of 4.50×10^6 rads/hour was used for all irradiations, since previous studies had confirmed that dose, and not dose rate, is the more critical consideration.

In all analyses, quantitative sugar determinations were carried out using the Somogyi Copper Method (9, 21, 23). Intrinsic viscosity was found

by first dissolving the cellulose sample in cupriethylenediamine solvent (24)--then measurements were made using a calibrated Ostwald-Fenske Viscometer at four different concentrations. The data were then plotted, the curve extrapolated to zero concentration and the intrinsic viscosity read as the ordinate intercept.

The cellulose samples to be irradiated were contained in polyvials which were placed in cadmium foil-lined aluminum tubes. Each tube was fitted with a screw cap containing a cadmium gasket to insure a minimum of water leakage when the capsules were in the pool. The tubes were placed in an aluminum tube rack which was lowered into a cadmium bucket opposite the reactor core.

Four sets of samples were prepared for each irradiation run. Each set consisted of two one-gram samples, weighed to ± 0.1 mg and placed in separate polyvials. A moisture determination was made on the remaining portion of filter paper from each set. In all cases the moisture content of the cellulose samples was around 5.0%. This was well above the 0.3% moisture levels at which Clegg and Kertesz (8) found an "after-effect".

After irradiation, the cellulose samples were taken from the polyvials and subjected to acid hydrolysis for durations of 0.5, 2, 4, 10 or 20 hours. As previously mentioned, hydrochloric acid of 0.4%, 1.6%, 3.75%, or 7.5% strength was used for the hydrolysis runs. The studies were made at temperatures of 25°C, 50°C and 90°C. Viscosity and sugar measurements were made on all the nonirradiated hydrolysis runs, the nonhydrolyzed irradiation runs and the hydrolyzed irradiation runs.

IV. RESULTS OF HYDROLYSIS STUDIES

The first studies were performed with irradiation doses of 2, 5 and 10 megarads, hydrochloric acid strength of 0.4% and 1.6%, temperatures of 25°C, 50°C and 90°C with hydrolysis times of 0.5, 2 and 4 hours. All showed marked decreases in the intrinsic viscosity and the mathematically related degree of polymerization (7) from the values found for the untreated cellulose samples. This decrease was from $(\eta) = 4.25$ cp and DP = 789 to $(\eta) = 1.10$ cp and DP = 209 for samples receiving an absorbed dose of 10×10^6 rads. This gives evidence to the theory that irradiation has a degrading effect on the chain structure of cellulose.

The nonirradiated hydrolysis runs gave little or no yield of glucose for either the 25°C or the 50°C studies. Those made at 90°C resulted in measurable but small (4.7%) glucose formation. This increase in glucose, produced at the higher temperature, suggests that the polymer becomes swollen--thus permitting easier access to the interior of the less crystalline regions. This swelling is due in part to the breaking of the hydrogen bond structure of the molecule causing subsequent decomposition. Previous investigators (19) of cellulose hydrolysis recognized that the sugars produced from cellulose were subject to decomposition on continued exposure to hot acid. Here, it was found that this decomposition is not unique to the hot acid range they studied (170°-190°C). Intrinsic viscosity measurements were made on a nonhydrolyzed sample which received a radiation dose of 10 megarads and on a hydrolyzed sample (0.4% acid at 50° for 4 hours) receiving the same dose. The viscosities for these two samples were identical, while the amount of glucose produced decreased from 1.5 to 0.32%.

Hydrolysis had no effect on the degree of polymerization of the cellulose, supporting the assumption that dilute acid is incapable of catalyzing the degradation of cellulose in its highly crystalline regions. It would seem therefore, that the acid produces glucose from the amorphous regions of the cellulose, while simultaneously decomposing glucose to substances of indefinite composition. After a time when all of the glucose able to be produced is formed, the decomposition reaction becomes predominant and possibly even the sole chemical occurrence taking place. Changes of

hydrolysis temperature and duration on the percentage yield of glucose showed some interesting effects. For hydrolysis durations of 0.5, 2 and 4 hours (1.6% acid, 10 x 10^6 rads), the percentage yield decreases as the temperature increases from 25°C to 50°C and then increases with a further increase in temperature (see Table I). At 25°C no appreciable chemical change takes place. At 50°C glucose decomposition plays a key role. Apparently at 50°C, the cellulose does not swell enough to allow the easy access to its interior regions so that there is a low limit to the possible glucose production and then degradation takes over.

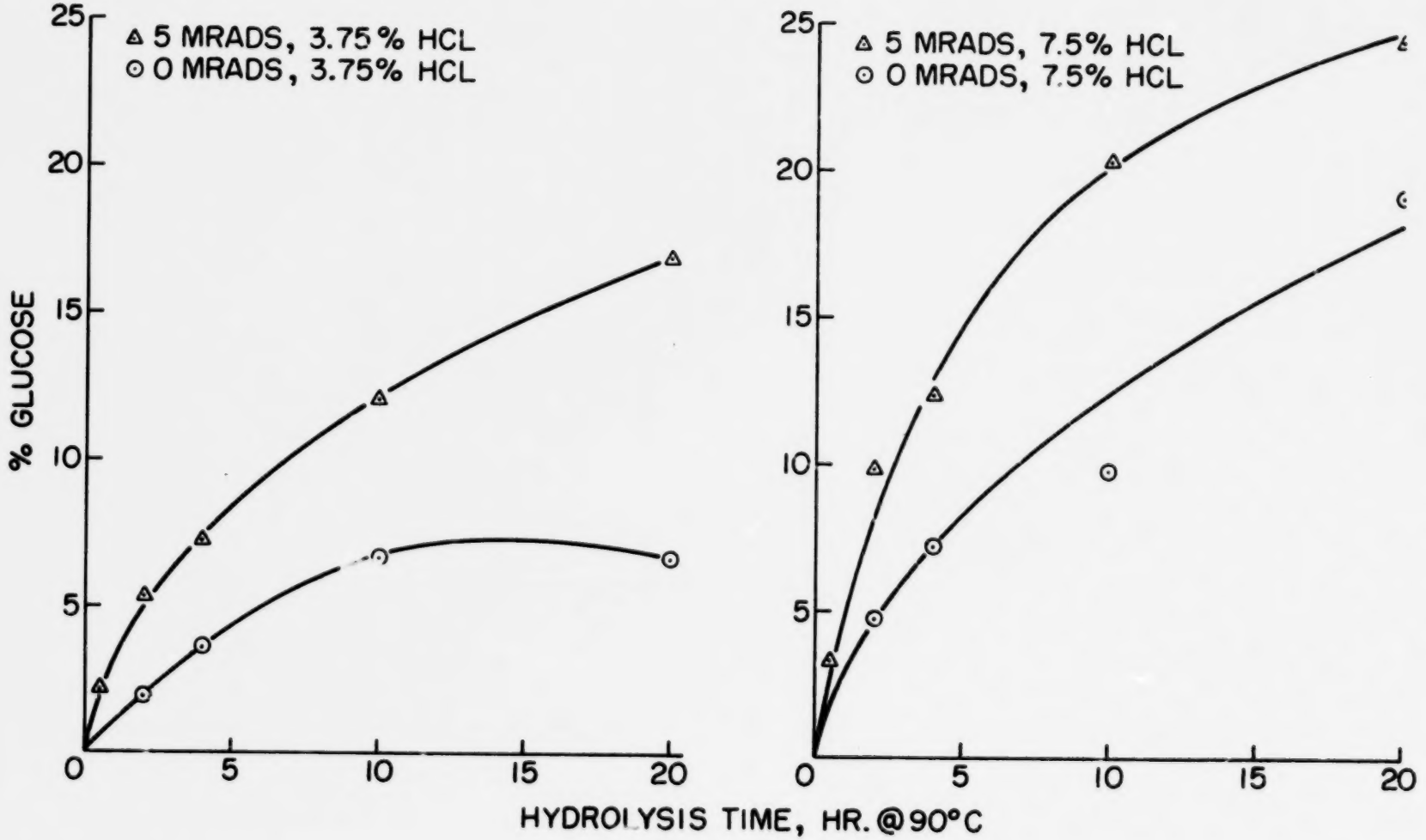
At the highest temperature studied, 90°C, the glucose reduction effect was not observed. The percent sugar produced seemed to level off somewhat after two hours of hydrolysis time. Suggested again is the argument that the higher temperature causes swelling and consequently facilitated access to the less crystalline regions of cellulose.

Although an increase in percent yield of glucose is brought about by an increase in acid strength, as well as by an increase in the radiation dose, the combined effects do not give significant production of glucose, even at a temperature of 90°C (< 5.0%).

On the basis of these first studies, a second series of combined radiation and hydrolysis experiments was carried out. All hydrolyses in the next series were performed at 90°C. Only 5 and 10 megarad doses were investigated because lower doses showed little improvement over no irradiation at all, and higher doses would prove difficult to obtain on a practical scale. Acid strengths were increased to 3.75% and 7.5%. Hydrolysis durations were the same as before with added times of 10 and 20 hours. Some of the results of these runs are plotted in Fig. 1. Thus, at 90°C and for the higher acid strengths, the sugar yields became well-behaved and predictable. The variance of yield with respect to hydrolysis duration and acid strength, became somewhat linear. The longer hydrolysis times and higher acid strengths gave the expected higher sugar yields (17-25%). There was no evidence of glucose decomposition as the controlling reaction for any of the durations for either of the acid strengths or doses studied in this second set.

Table I. Irradiated Hydrolysis Runs Using 1.6% HCl, 10×10^6 rads.

TEMPERATURE (°C)	HYDROLYSIS TIME (Hours)	% GLUCOSE
25	0.5	1.64
25	2.0	2.32
25	4.0	2.64
50	0.5	1.24
50	2.0	0.98
50	4.0	0.48
90	0.5	2.31
90	2.0	4.34
90	4.0	4.89


△ 5 MRADS, 3.75% HCL
⊙ 0 MRADS, 3.75% HCL
% GLUCOSE
25
20
15
10
5
0
5
10
15
20
△ 5 MRADS, 7.5% HCL
⊙ 0 MRADS, 7.5% HCL
HYDROLYSIS TIME, HR. @ 90°C

The dose needed to effect significant conversion of cellulose to glucose is a heavily weighted factor in the determination of the industrial feasibility of this reaction. Obviously, the lower the dose needed to attain the sought after conversion levels, the more attractive the process will be. It was observed at the highest acid strength studied in this second series of experiments that doubling the dose from 5 to 10 megarads provided little improvement in the sugar yield. (Refer to Table 2.) This leads to the conclusion that, for these acid concentrations and hydrolysis temperatures, maximum glucose production may be achieved with a gamma ray dose of 5 megarads or less.

A third series of experiments was performed in which the effects of several parameters on glucose yields were studied. First, the hydrochloric acid concentration was increased to 15% for all hydrogen (which were performed at 90°C). Second, another form of cellulose (namely, cotton) was studied in addition to the paper of the previous series. Last, the effects of small additions of sodium nitrite to the cellulose prior to irradiation were examined. This last aspect was suggested by a recent disclosure (20) that such a treatment can significantly enhance the degradation process. Unfortunately, this last series of experiments was begun after the University of Virginia Reactor (UVAR), the source of gamma ray radiation, was shut down for extensive modifications. For these experiments the only source of gamma ray radiation was the decay radiation from the "hot" fuel elements stacked in a non-critical configuration at one end of the pool. Consequently, the gamma ray dose rates attainable with this source varied over a range of values, all at least one order of magnitude less than the dose rates in the first two series of experiments. The resulting glucose yields exhibited very little uniformity or predictability. It is believed that the wide variation in dose rates was responsible for the large amount of scatter in the glucose data.

At all radiation levels tested, hydrolysis durations of 4 hours or less showed little physical effect on the filter paper samples, aside from increased ease in tearing. This observation held for all temperatures and acid strengths. For longer hydrolysis times the samples became discolored

Table 2. Irradiated Hydrolysis Runs Using 7.5% HCl at 90°C.

HYDROLYSIS TIME (Hours)	DOSE (Megarads)	% GLUCOSE
0.5	5	3.29
2.0	5	9.87
4.0	5	12.44
10.0	5	20.23
20.0	5	24.44
0.5	10	2.96
2.0	10	9.06
4.0	10	12.18
10.0	10	21.14
20.0	10	27.19

and pasty and they lost completely the appearance of filter paper. This is the preliminary effect seen in the formation of the aforementioned humic substances.

V. CONCLUSIONS

The irradiation of cellulose material with gamma rays prior to acid hydrolysis can produce a significant increase in the glucose yield relative to non-irradiated cellulose. However, for the range of conditions investigated in this study, a maximum conversion of cellulose to glucose of about 27% was obtained. A yield of this magnitude is probably too small to be of practical value for a large-scale commercial process.

In the range of temperatures considered (25 to 90°C), glucose yields inveased with temperature, all other parameters being equal.

In the range of acid concentrations considered (0.4 to 7.5% HCl), glucose yields increased with acid concentration, all other parameters being equal.

Gamma ray doses of 2, 5, and 10 megarads were administered at a dose rate of about 4.50×10^6 rads/hour. For the hydrolysis conditions considered (0.4 to 7.5% HCl and 25 to 90°C) doses of less than 2 megarads enhanced glucose yields only slightly. A dose of megarads produced significant increases in glucose yields, whereas a 10 megarad dose produced little improvement relative to a 5 megarad dose. Thus, it can be concluded that for the hydrolysis conditions studied, a radiation dose of 2 to 5 megarads results in maximum glucose yields.

VI. SUGGESTIONS FOR FURTHER STUDY

The effects of dose rate as well as dose on the radiolytic hydrolysis of cellulose should be studied.

The effects of higher acid concentrations (> 7.5% HCl) and higher hydrolysis temperatures (> 90°C) should also be studied.

Finally, the effectiveness of treatment of the cellulose with a sodium nitite solution prior to irradiation should be studied.

VII. PUBLICATIONS

Most of the work performed under this grant is reported in detail in the following M.S. Thesis: "The Effect of Gamma Radiation on the Hydrolysis of Cellulose," by Nance K. Dicciani, University of Virginia, 1970.

A paper is being submitted to Nuclear Applications, summarizing the work reported in the above thesis.

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